

HYDROCONVERSION CHARACTERISTICS ON NARROW FRACTIONS OF RESIDUA

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ABSTRACT

An atmospheric residuum from Dagang crude of China(DGAR) and two vacuum residua from Arabian Light crude and Arabian Medium crude(SQVR and SZVR) were fractionated into 7-8 cuts by supercritical fluid extraction fractionation (SFEF) technique developed by State Key Laboratory of Heavy Oil Processing. The major properties of these fractions were measured, and each fraction was catalytically hydroprocessed in a 100 mL autoclave with crushed commercial Ni-Mo catalyst at the same reaction conditions. Removal of sulfur and nitrogen decreases with increase of the average molecular weight(AMW) of the feedstock, but the total conversion of heavy portion greater than 500 for every fraction is similar. The yield of coke increases with increasing AMW of feed, especially for the several heavier fractions, and the SFEF residue inhibits the HDS and HDN of other SFEF fractions to a certain extent.

INTRODUCTION

Due to increasing use of heavy oils and bitumen as refinery feedstock and the growing demand of light distillate oils, catalytic hydroprocessing of heavy oil plays an increasingly important role in modern petroleum deeply processing. Considerable effort has been focused worldwide on characterizing oils from the points of view of feedstock properties and the resultant kinetic properties. Much of this effort, however, has been directed at characterizing the reaction kinetics of whole oils, and the investigations about the hydroconversion features of narrow fractions of heavy oils are scarce. Hoog(1950)^[1] upgraded two narrow-boiling fractions and a whole gas oil, all at 375°C with a Co/Mo catalyst. The rate of desulfurization decreased with increasing boiling point. Yitzhaki and Aharoni(1988)^[2] processed a whole gas oil and fractionated the feed and products into narrow-boiling cuts. The desulfurization kinetics were estimated for each fraction based on the assumption that no sulfur compounds migrated between fractions. Their modeled kinetics showed that the HDS rate decreases with the increase of average boiling point of the feed. Constantine Philippopoulos and Nickos Papayannakos(1988)^[3] investigated the hydrocracking reaction of asphaltene from an atmospheric residuum and the HDS kinetics and diffusion properties of asphaltene and deasphaltene oil(DAO) of the atmospheric residuum in a small trickle-bed reactor. The hydrocracking of asphaltene and the HDS of DAO were elucidated very well with second order kinetic equations, the HDS reaction of asphaltene was represented by third order kinetics. The effective diffusivity of DAO is 5.85 times as big as that of asphaltene and the HDS rate of DAO is obviously faster than that of asphaltene. Trytten and Gray(1990)^[4] fractionated a heavy gas oil, produced by thermal cracking of Athabasca bitumen, into six narrow boiling cuts of nominal 50° width and a high boiling residue, and catalytically hydroprocessed them in a 150 mL CSTR with a commercial Ni/Mo catalyst. The AMW of the fractions range from 197 for the lightest one to 653 for high-boiling residue. The reaction conditions were $P_{H_2}=13.9\text{MPa}$ $V_{H_2}=1.05\text{L/min}$ $HSV=12.5\text{ml/(hg)}$. Reaction results were treated by first order kinetics. The removal of sulfur and nitrogen as well as conversion of aromatic carbon decrease with the increase of feed AMW. The intrinsic activation energies of HDN and HDS do not change significantly with increasing feed AMW, but the apparent activation energies increase gradually. The estimated effectiveness factors increase with the increase of feed AMW for both reactions and pass through a maximum at a molecular weight of 362 for the feed. The reactivity decreasing of the sulfur and nitrogen with increasing feed AMW due to the steric effects or inhibition by components in the mixture plays a dominant role on the decrease of effectiveness factors for lighter fractions, although the estimated diffusivity decreases gradually.

Dai^[5] fractionated the Shengli Vacuum residuum into 14 cuts by the SFEF technique and separated each fraction into saturate, aromatics and resin by SARA method. Every resin in different fraction was catalytically cracked in a small reactor designed oneself. When the total yield of extract oil in SFEF is not greater than 78%, the resin in each fraction can be

cracked easily with a liquid yield of 65-75%. The reactivity of resin is greatly affected by its AMW, the greater the AMW of resin is, the poorer its cracking reactivity.

As a whole, the reaction features of feed vary with the AMW, or molecular size. Now there are not investigations about the hydroconversion characteristics of narrow fractions of residuum reported for lack of proper separation method. The SFEF technique developed by State Key Laboratory of Heavy Oil Processing affords the possibility to do such a work. In this paper, three residua were fractionated into narrow fractions by the SFEF method and all fractions were catalytically hydroprocessed at the same conditions.

EXPERIMENTAL

Feedstocks. Two vacuum residua of Arabian Light crude and Arabian medium crude were provided by Fushun Research Institute of Petroleum Processing, and Dagang atmospheric residuum came from Dagang refinery. Such three residua were separated respectively into 8 fractions by the SFEF method. The main properties of each fraction were measured and summarized in table 1.

Table-1 SFEF fraction properties of residua

DGAR, iso-butane as solvent in SFEF									
Fraction No.	1	2	3	4	5	6	7	8	residue
Fraction, m%	10.26	11.10	10.30	10.65	9.98	10.27	10.07	10.54	16.83
Sum, m%	10.26	21.36	31.66	42.31	52.29	62.56	72.63	83.17	100.0
20° density, g/cm ³	0.8721	0.8793	0.8855	0.8905	0.8960	0.9027	0.9103	0.9267	1.0616
Molecular weight	353	379	407	420	443	467	505	582	1473
S m%	0.101	0.112	0.149	0.152	0.176	0.197	0.234	0.315	0.780
N µg/g	436	1119	1430	1770	2066	2398	2940	3841	12979
H/C, mol/mol	1.81	1.80	1.78	1.77	1.75	1.73	1.71	1.66	1.39
SQVR, normal pentane as solvent in SFEF									
Fraction No.	1	2	3	4	5	6	7	8	residue
Fraction, m%	9.9	10.2	10.1	10.0	10.1	10.1	10.0	12.0	18.3
Sum, m%	9.9	20.1	30.2	40.2	50.3	60.4	70.4	80.4	98.7
20° density, g/cm ³	0.9432	0.9559	0.9634	0.9714	0.9789	0.9947	1.0232	1.0606	
Molecular weight	558	610	644	653	690	744	900	1128	3047
Carbon residue m%	2.2	6.1	6.2	6.5	8.4	12.6	15.4	26.8	33.1
S m%	2.55	2.60	2.94	3.20	3.48	4.11	4.74	5.56	5.89
N µg/g	1845	2088	2550	2823	3000	3863	5356	6100	8100
H/C, mol/mol	1.67	1.62	1.63	1.63	1.59	1.55	1.46	1.38	1.14
SZVR, normal pentane as solvent in SFEF									
Fraction No.	1	2	3	4	5	6	7	8	residue
Fraction, m%	10.2	10.2	10.2	10.0	10.2	10.0	9.9	5.0	24.6
Sum, m%	10.2	20.4	30.6	40.6	50.8	60.8	70.7	75.7	100.3
20° density, g/cm ³	0.9369	0.9484	0.9610	0.9740	0.9937	1.0056	1.0320	1.0533	1.1405
Molecular weight	498	611	657	711	802	826	1079	1124	3394
Carbon residue m%	3.0	4.0	4.8	6.8	10.3	14.5	21.3	27.0	44.8
S m%	2.70	2.71	2.92	3.54	4.18	4.41	4.83		6.40
N µg/g	2169	2490	3280	3950	4600	5803	7132		9700
H/C, mol/mol	1.69	1.66	1.64	1.63	1.56	1.51	1.47		1.19

Catalyst. A key catalyst used in Chevron VRDS process(CAT1) and another catalyst(CAT2) produced in China were chosen in this research, their major properties were listed in table 2. The average pore diameter of both catalysts is 30Å - 40Å, pore volume is 0.39 - 0.45mL/g, and specific surface area is 203 - 275 m²/g. The main metal active components are molybdenum and nickel. Catalyst was crushed and sieved into 60/80 mesh particles (average diameter of 0.35mm), and the catalyst particles were presulfurized before use in reaction.

table-2 Major properties of catalysts

	CAT1	CAT2
Particle size/ mm	0.79	0.84
Particle density/ g/cm ³	1.52	1.50
Bulk density/ g/cm ³	0.89	0.88
Specific area/ m ² /g ⁻¹	275	203
Pore volume/ mL/g ⁻¹	0.45	0.39
Pore radius/ Å	33	38
Active components	Mo, Ni, Fe, Co	Mo, Ni, Fe,
support	γ-Al ₂ O ₃	γ-Al ₂ O ₃

Hydroconversion and Separation.

The flowsheet of heavy oil hydroconversion and separation was shown in figure 1. The crushed catalyst was presulfurized firstly, washed with solvent and dried in a vacuum drying oven. The presulfurized catalyst and sample were charged into the autoclave with the ratio of 1 to 10. After loading the catalyst and sample, the system was purged with hydrogen three times, then the temperature was increased gradually and the agitator was switch on when the temperature reached from 100°C - 150°C. Standard reaction conditions include a temperature of 400°C, initial hydrogen pressure(IHP) of 8.5Mpa at ambient temperature, and stirring rate of about 850rpm. After reaction, the autoclave was taken out from the heating furnace and put it into cooling water. When the temperature reaches to about 200°C, the reactor was placed into an isothermal water bath of 60°C in order to assure the consistency of sampling conditions and avoid or reduce the evaporation of light components in liquid product. While the autoclave comes to about 60°C, reactor was connected to a gas ration and sampling system for collecting gas product. The in-situ temperature, atmospheric pressure and the collected gas volume were recorded. Then the gas product was transferred into a gas sample bag for composition analysis. After sampling gas, the reactor was cooled down to ambient temperature, opening the reactor and taking immediately a little liquid product into a centrifugal test tube. The catalyst contained in the liquid product was deposited on the bottom of the test tube by centrifugation separation in a centrifugal machine at 5000rpm for 5 minutes. The upper oil in test tube was transferred to a sealed vial for simulated distillation analysis.

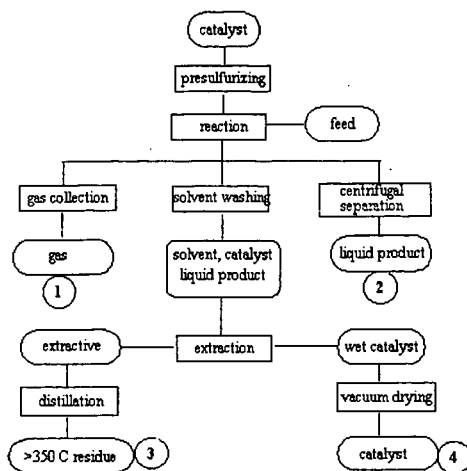


Fig.1 Hydroconversion and separation flowsheet

When the temperature reaches to about 200°C, the reactor was placed into an isothermal water bath of 60°C in order to assure the consistency of sampling conditions and avoid or reduce the evaporation of light components in liquid product. While the autoclave comes to about 60°C, reactor was connected to a gas ration and sampling system for collecting gas product. The in-situ temperature, atmospheric pressure and the collected gas volume were recorded. Then the gas product was transferred into a gas sample bag for composition analysis. After sampling gas, the reactor was cooled down to ambient temperature, opening the reactor and taking immediately a little liquid product into a centrifugal test tube. The catalyst contained in the liquid product was deposited on the bottom of the test tube by centrifugation separation in a centrifugal machine at 5000rpm for 5 minutes. The upper oil in test tube was transferred to a sealed vial for simulated distillation analysis.

The remaining liquid product and catalyst in reactor was diluted with solvent and transferred into a Soxhlet apparatus, then extracted with dichloro-ethane for one hour, finally the extracted liquid should be not color. The wet catalyst in the extractor was taken out and placed into a vacuum drying oven to dry for coke content and other properties analysis. The extractive was distilled at atmospheric pressure to recover the solvent, then the liquid product was transferred into a small distillation flask of 150mL and subjected to vacuum distillation to obtain the high boiling residue of >350°C for analyzing the sulfur and nitrogen contents, molecular weight, and hydrocarbon group composition.

In the present study, the loss in experiment could be ignorable and sum of yields of gas, coke and liquid product accounted as 100%. Once the gas and coke yields are determined, the yield of any distillate can be calculated according to the simulated distillation data of liquid product.

RESULTS AND DISCUSSION

Hydroconversion of DGAR fractions. It is shown in table 3 that the removal of sulfur and nitrogen are similar for both catalysts. The HDS conversions are very high for No.1 to No. 8 fractions, all greater than 90%. The HDN conversion is greater than 75% for fraction lighter than No.7 fraction. HDS and HDN conversions decrease obviously with the increase of AMW of feed, and the declining rate for HDN is greater than that for HDS. The removal of sulfur and nitrogen in the SFEF residue is more difficult than other fractions, the conversion of HDS and HDN are only 44.3% and 16.4% respectively.

From the distribution of cracked product, the gas yield of each fraction do not change obviously except for the SFEF residue. In the latter case, the short side chains may be directly cracked into gas product, which results in the high gas yield. The yields of gasoline and diesel distillates lower with increasing the AMW of SFEF fractions. The distribution of product trends towards two ends for the SFEF residue, than is, gas and coke are produced greatly, which is same as the

features of polyaromatics cracking. It also can be seen that the coke yield increases gradually with the fraction becoming heavier. The coke yield of SFEF residue is about 4 times larger than that of No.8 fraction and 13 times as big as that of No.1 fraction.

Hydroconversion of SZVR and SQVR fractions. It is shown from the data in table 3 that the reactivity of HDS and HDN for SFEF fractions of SZVR and SQVR is obviously poorer than that of DGVR. Most of HDS conversions is less than 70%, and the HDN conversion is less than 60% for all fractions. This could be ascribed to the higher boiling point, larger molecular weight and stronger aromaticity of SZVR and SQVR compared with DGAR and most of sulfur and nitrogen atoms existing in the heterocyclic structures, which results in the difficulty of HDS and HDN reactions.

In general, the gas and coke yields increase with the fraction becoming heavier, although some experimental points fluctuate due to experiment and analysis errors. There is not coincident trend for the distribution of liquid product. The gas and coke yields increase seriously compared with other fractions.

Table-3 Hydroconversion results (400°C, 240 min, IHP of 8.5MPa)

SFEF fractions of DGAR									
feed	DGAR-1	DGAR-3	DGAR-5	DGAR-7	DGAR-2	DGAR-4	DGAR-6	DGAR-8	residue
catalyst	CAT1	CAT1	CAT1	CAT1	CAT2	CAT2	CAT2	CAT2	CAT1
S removal, %	96.3	95.0	94.7	91.6	95.8	94.4	93.4	90.7	44.3
N removal, %	95.2	87.6	79.1	60.9	94.9	84.8	76.1	48.3	16.4
Material balance, %									
gas	1.13	0.87	1.18	0.71	1.18	1.07	0.96	0.96	1.58
<200°C	7.76	6.94	5.37	3.96	5.37	4.93	3.65	3.89	7.21
200-350°C	37.81	24.86	19.76	14.49	22.94	18.92	14.28	12.76	10.47
350-500°C	53.10	60.65	59.66	49.14	61.89	58.51	52.51	39.27	27.01
>500°C	0.00	6.41	13.75	31.36	8.35	16.23	28.23	42.58	51.12
coke	0.20	0.27	0.29	0.33	0.27	0.36	0.38	0.56	2.60
SFEF fractions of SZVR									
feed	SZVR-1	SZVR-3	SZVR-5	SZVR-7	SZVR-2	SZVR-4	SZVR-6	residue	DGAR
catalyst	CAT1	CAT1	CAT1	CAT1	CAT2	CAT2	CAT2	CAT1	CAT1
S removal, %	92.5	70.9	51.1	31.0	85.9	75.7	54.0	27.4	78.1
N removal, %	59.8	42.2	20.2	13.3	53.7	38.0	19.7	7.4	41.9
Coke on Cat, %	4.56	5.59	10.74	15.69	6.06	8.19	11.78	23.74	
Coke amount, g	0.22	0.27	0.54	0.84	0.29	0.40	0.60	1.40	
Coke yield, %	0.49	0.60	1.22	1.87	0.64	0.89	1.33	3.11	
Material balance, %									
gas	1.22	1.18	2.24	3.13	0.49	0.93	2.07	3.16	
<200°C	8.70	7.14	11.24	12.32	7.83	8.61	9.60	2.95	
200-350°C	22.69	17.46	22.34	20.43	18.62	18.87	17.96	12.90	
350-500°C	42.72	31.02	29.18	21.32	32.92	29.54	24.65	15.90	
>500°C	24.18	42.60	33.79	40.92	39.50	41.16	44.38	61.98	
coke	0.49	0.60	1.20	1.87	0.64	0.89	1.33	3.11	
SFEF fractions of SQVR									
feed	SQVR-2	SQVR-4	SQVR-6	SQVR-8	residue	SQVR	SQVR		
catalyst	CAT1	CAT1	CAT1	CAT1	CAT1	CAT1	CAT2		
S removal, %	78.3	70.8	61.0	48.2	23.8	48.1	52.3		
N removal, %	31.2	24.8	15.3	5.5					
Coke on Cat, %	8.01	7.34	9.94	13.84	28.75	18.45	14.77		
Coke amount, g	0.44	0.40	0.55	0.80	1.81	1.02	0.78		
Coke yield, %	0.88	0.80	1.10	1.60	4.02	2.27	1.73		
Material balance, %									
gas	1.02	0.98	1.34	2.04	2.89	1.29	1.47		
<200°C	9.04	8.32	6.57	11.00	2.81	6.28	5.14		
200-350°C	16.88	16.00	16.79	14.57	11.46	14.43	12.91		
350-500°C	31.35	29.43	28.17	19.47	12.33	25.73	22.21		
>500°C	40.83	44.47	46.03	51.32	66.49	50.01	56.54		
coke	0.88	0.80	1.10	1.60	4.02	2.27	1.73		

Relation of coke yield and feed properties. Coking trend is an important factor of feed processing characteristics, it affects not only the activity and selectivity of catalyst and the distribution of product, but also the increase of bed pressure drop of reactor, energy consumption and the operation period. Coke yield increases with the increase of aromatic carbon fraction, f_a , in the average molecule, and is directly proportional to the content of resin and asphaltene in

feed, x_{RA} . The fitting equations are as follows,

$$y_{\text{coke}} = 8.076 \cdot f_a^{1.495} \quad (1)$$

$$y_{\text{coke}} = 0.05049 \cdot x_{RA} + 0.1776 \quad (2)$$

Where y_{coke} is the coke yield, wt%. The coking characteristics can also be represented by the heavy oil characteristic parameter, K_H , which is defined as,^[6]

$$K_H = 10 \cdot \frac{H/C}{AMW^{0.1236} \cdot d_4^{20}} \quad (3)$$

Where H/C is the atomic ratio of hydrogen to carbon, d_4^{20} is the relative density. With the decrease of feed K_H , coke yield increases slowly when $K_H=6.0-8.0$, the increasing rate of coke yield rises gradually with decreasing the feed K_H value, and grows seriously for $K_H < 6.0$. Such a relationship can be represented by the following equation,

$$y_{\text{coke}} = 444.5 \cdot K_H^{-3.23} \quad (4)$$

Relations of HDS & HDN reactivity and feed properties. The HDS and HDN conversions decrease quickly with the increase of the content of resin and asphaltene, and the decrease of atomic ratio of hydrogen to carbon. This suggests that it is more difficult to remove the sulfur and nitrogen atom in the heavier component. Figure 2 shows the relationships between the percentages of sulfur and nitrogen removal and the heavy oil characteristic parameter. With decreasing the K_H value, the removal of nitrogen decreases quickly when the K_H is bigger, and gradually tends towards a constant level which approximates the conversion for thermal cracking reaction. While $K_H > 8.0$, the declining rate of HDN reaction is faster than that of HDS reaction. This relationship behaves as S-type curve for HDS and as an ice stick for HDN. The HDS conversion is always greater than that of HDN for any fraction at the same reaction conditions. This implies that the reactivity of HDS and HDN lowers obviously with the increase of fraction AMW, and the removal of nitrogen is more difficult than that of sulfur.

The solid circle and bold plus sign are the data points of whole DGAR HDN and HDS. The K_H value of DGAR is 9.1, the responding HDS and HDN conversions predicted from the curves in figure 2 are 94% and 77% respectively, but the real HDS and HDN conversion are 71.0% and 41.9% respectively. This shows that the heavy components in residuum may inhibit the HDS and HDN reaction of lighter components to a certain extent. Due to the strong adsorptivity and high coking trend, these heavy components would affect the activity of catalyst and then decrease the catalytic reaction rate.

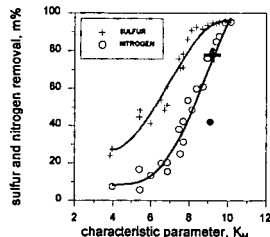


Fig.2 sulfur and nitrogen removal versus K_H

Comparing the HDS and HDN results for CAT1 catalyst with those for CAT2 catalyst shown in table 3, it is found that CAT1 has a similar HDS and HDN activity with CAT2 for lighter SFEF fractions, but for heavier fractions the latter has stronger catalytic activity than the former. This phenomenon may be attributed to the larger pore size of the CAT2 catalyst.

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